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# Tracking the first steps of aerosol nucleation with subnanometer-sized particles

Aerosol particles represent one of the most important, yet perhaps least understood, components of our atmosphere. They have long been recognized as the key players in the Earth's atmosphere, with an indisputable effect on the global climate. These particles also provide a playground for heterogeneous reactions and have a negative impact on human health, particularly in polluted areas. They affect the climate as strongly as the greenhouse gases, but in the opposite way, i.e., acting to cool the Earth by reflecting solar radiation and forming clouds [1]. Aerosols are one of the most uncertain factors in climate change projections because they come from many sources, form in different ways, and span a huge range of lifetimes in the atmosphere from seconds to days and years. Aerosol particles are either emitted directly into the atmosphere (primary aerosols) or formed in the atmosphere from precursor gases (secondary aerosols). Nearly half of the cloud seeds in nature are thought to originate as secondary aerosols through gas-to-particle conversion upon depositing gaseous molecules on existing particles or by condensing molecules one by one [1]. As shown in Fig. 1, the formation of these particles in the atmosphere begins with molecular clusters that may be stabilized, for example, by acid–base reactions or hydrogen bonding, and grow by incorporating gas-phase molecules until they become large enough to serve as cloud condensation nuclei.

Small (sub)nanometer-sized particles, however, cannot be detected directly in the atmosphere [2]. Therefore, all nucleation experiments are conducted exclusively in laboratories using aerosol chambers or flow reactors, in which the initial stages of the formation of small aerosol particles are modeled under precisely controlled experimental conditions [1]. Aerosol chambers are closed environments that replicate atmospheric conditions by controlling temperature, humidity, and gas composition. Within these experiments, specific gases and precursor molecules are introduced into the chamber, initiating particle formation and growth, which are systematically monitored over time. Flow tubes, on the other hand, are open systems in which gases and aerosol precursors are introduced into a flowing gas stream. As the gas flows through the tube, particles form and grow under controlled conditions, and their properties can be measured at various points along the length of the tube. Flow-

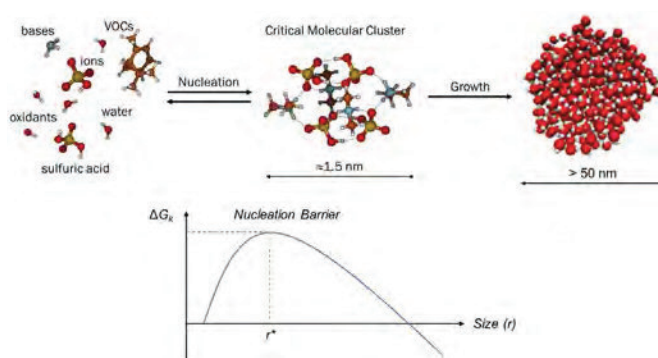


Fig. 1: Illustration of the nucleation pathway from gas-phase molecules to aerosol particles, with the free energy profile shown as a function of particle size.

tube systems are essentially equivalent to condensation systems, with the time scale in the latter converted to a length scale in the former. A combination of these laboratory experiments with field measurements has enabled the identification of nearly all aerosol nucleation precursors, including sulfuric acid, bases like ammonia and alkylamines, and oxidized organic compounds [1]. Furthermore, this approach has generated essential kinetic data on aerosol nucleation, which supports the improvement of climate model accuracy.

Despite recent advances, laboratory experiments on aerosol nucleation face three main challenges [3]: (1) Detecting nucleating particles is challenging due to their fragility. Mass spectrometry, the most commonly used method, requires ionization, and even soft ionization may induce fragmentation, thereby altering the original cluster composition and size. (2) Nucleation occurs in chemically complex environments, which complicates the identification of key species, e.g., water is often missing from observed clusters, although it clearly plays a role in the nucleation process. (3) Extremely low precursor concentrations (at ppb–ppt levels) make the results highly sensitive to trace impurities. As a result, nucleation rates – even for simple systems like binary nucleation of sulfuric acid and water – can differ by several orders of magnitude across different studies, indicating that our understanding of these processes is limited [4].

There is, however, an alternative bottom-up approach, using subnanometer-sized particles (called clusters) in molecular and ion beams [5, 6]. These particles have a finite size and a defined number of molecules, making them ideal for tracking particle nucleation in the sub-nanometer size range with the highest atomic resolution. Although cluster beam studies, in contrast to macroscopic experiments, cannot fully simulate the

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complexity and equilibrium conditions of aerosol nucleation, they can provide detailed information at the molecular level about particle-molecule interactions, core stabilization mechanisms, and other related processes.

In these studies, nucleation can be probed in expansion or pickup experiments, where a single molecule is adsorbed on a pre-existing cluster. Another approach, especially well-suited to investigate ion-induced nucleation, involves kinetic measurements in ion traps, where mass-selected ions interact with neutral precursors. This allows for detailed analysis of nucleation pathways and the determination of the corresponding rate coefficients. Given that neutral-neutral nucleation is the dominant pathway in the atmosphere, the following section highlights how the pickup experiments shed light on the mechanisms of new particle formation.

In pickup experiments, clusters are formed in the supersonic expansion, but in contrast to a Laval-nozzle expansion, the cluster formation ceases shortly after the nozzle, and the resulting clusters fly isolated in a vacuum. The cluster beam is then introduced into a pickup cell filled with a dilute gas, where gaseous molecules undergo individual collisions with the clusters and can stick to their surface. The efficiency of this process is reflected in the uptake cross section, which is determined by combining mass spectrometric analysis of cluster fragments with velocity measurements [7]. Nucleation rates should, in principle, be derived from uptake cross sections, but direct comparison between the methods is challenging without measurements in atmospherically relevant conditions and a clear understanding of evaporation processes. A clear correlation has been observed, for example, in the homogeneous nucleation of water clusters. Pickup experiments revealed that the cross section for the pickup of  $\text{H}_2\text{O}$  molecules on a water cluster (with  $R \approx 1.2$  nm) is more than twice as large as their calculated geometrical cross section due to long-range interactions. On the other hand, Laval expansion studies showed that the monomer association rates were enhanced by a factor of 4–5 compared to the collision rates. Thus, both expansion and pickup experiments yield qualitatively consistent results [5].

Our earlier studies showed that the uptake of molecules by hydrated nitric acid clusters,  $(\text{HNO}_3)_m(\text{H}_2\text{O})_n$  – used as a proxy for ultrafine aerosol particles – is enhanced when volatile organic compounds (VOCs) are oxidized, compared to their parent VOCs such as  $\alpha$ -pinene or isoprene [8]. This increase in sticking efficiency was attributed to thermodynamic factors: oxidized compounds can form hydrogen bonds with the clusters, whereas the interactions of the parent VOCs are weaker and nonspecific. To demonstrate the capability of the technique to resolve unprecedented details – revealing not only thermodynamic effects but also the dynamics of the collision and uptake process – a systematic study was performed on the uptake of organic alcohols by  $(\text{HNO}_3)_m(\text{H}_2\text{O})_n$  clusters. A series of alcohols was carefully selected to investigate how uptake depends on carbon chain length (i.e., size, mass, and hydrophobicity), and to examine steric effects among different isomers [9].

Fig. 2 shows the relative uptake cross sections for the studied alcohols, with experimental data represented by bars and

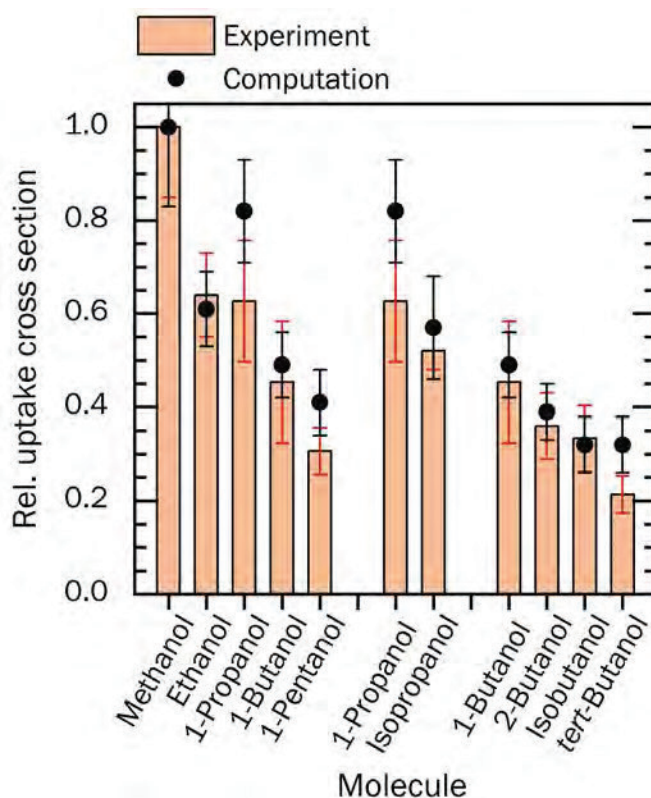


Fig. 2: Comparison of experimental and computational relative uptake cross sections for alkyl alcohols on hydrated  $\text{HNO}_3$  clusters.

simulation results by points. The excellent agreement between experiment and simulation suggests that the measured relative sticking probabilities are reliable. In general, uptake cross sections decrease with increasing alkyl chain length and greater steric hindrance near the OH group. It may seem surprising that the uptake cross section decreases with longer carbon chains, particularly if one expects uptake to scale with collision cross section. This trend can be rationalized by the higher momentum of heavier molecules, which can help them escape the attractive potential of the cluster. In addition, only one OH group is available for binding, and with longer chains, proper orientation becomes more difficult, resulting in lower sticking probabilities. This interpretation is further supported by the behavior of isomeric species, where branching increases the steric hindrance of the OH group by adjacent  $\text{CH}_2$  and  $\text{CH}_3$  units. A typical example is 1-butanol, which has an open linear structure and exhibits a cross section approximately twice as large as that of tert-butanol, which requires a specific orientation for the collision to result in uptake.

In addition, these experiments allow us to study the underlying chemistry and core stabilization mechanisms. Numerous nucleation studies have shown that humidity significantly affects nucleation rates, even though water is typically absent from the mass spectra. This is often explained by the fact that, although clusters are hydrated under atmospheric conditions, water molecules rapidly evaporate upon entering the mass spectrometer, where the hydration equilibrium can no longer be maintained in the ultrahigh vacuum. In contrast, cluster beam experiments begin with relatively well-defined hydrated acid clusters, onto which molecules are deposited; thus

enabling studies of particles that initially contain water. However, when dimethylamine (DMA) is taken up by small  $\text{HNO}_3/\text{H}_2\text{O}$  clusters, a complete loss of water molecules is observed [10]. The resulting cluster ions exhibit specific  $\text{HNO}_3$ -DMA pairing but contain no water. While the acid-base reaction is evident, its thermochemistry alone cannot account for the complete loss of water molecules; the ionization required for mass spectrometry detection likely contributes to the formation of anhydrous clusters [10].

These are just a few examples of how cluster-based experiments can help elucidate the dynamics involved in aerosol nucleation. Many more approaches exist – for example, collision-induced dissociation experiments are used to identify fragmentation channels of aerosol particles [11], and infrared action spectroscopy is applied to determine the structures of small clusters, intramolecular interactions, and bonding motifs that lead to stable particles [12]. Ion trap experiments can also provide size-dependent kinetic data on nucleation rates [13]. Overall, cluster studies now represent a powerful and viable approach for gaining detailed molecular-level insight into processes relevant to atmospheric particle formation.

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Jozef Lengyel studied chemistry at TU Bratislava and completed his PhD in physical chemistry in 2015 jointly at the Heyrovský Institute of the Czech Academy of Sciences and the University of Chemistry and Technology, Prague. He held postdoctoral positions at the University of Innsbruck (Lise Meitner Fellow, 2016–2017) and TU Munich (Alexander von Humboldt Fellow, 2018–2020). He established a junior research group at TU Munich in 2021 with support from the DFG Emmy Noether Program and completed his habilitation in physical chemistry in 2025. His research focuses on particle nucleation and the reactivity of hydrated ions and clusters, with emphasis on atmospheric chemistry and catalysis, employing molecular and ion beam techniques, advanced mass spectrometry, laser spectroscopy, and quantum chemical calculations.

